Multi-layer hollow body, method for manufacturing such a hollow body, and compression-blow-moulding mould

5 The present invention relates to a hollow body made of plastic of multi-layer polymeric structure.

Hollow bodies made of plastic of multi-layer polymeric been developed structure have to meet 10 requirements which demand properties which cannot be conferred by a single thermoplastic. This technique has been used In particular when the issue is one manufacturing hollow bodies made of plastic which have both high rigidity at ordinary temperature and good impermeability to liquids and gases they are intended 15 to contain. In this case, the impermeability function is generally provided by a layer internal to the structure, of very small thickness and low mechanical strength, which is made of a material which behaves 20 like a barrier to the liquids and gases contained in the hollow body.

One technique for producing hollow bodies made of plastic of multi-layer polymeric structure currently consists in assembling two or more elements of similar multi-layer structure, by welding.

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We are also witnessing a significant reduction in the permissible amounts of liquid and vapour which can escape into the environment from containers containing organic substances. In the field of fuel tanks, new standards imposing extremely low levels of permissible losses will very soon come into force.

In hollow bodies manufactures as described above by assembling welded multi-layer elements, the region of the welding planes has lessened impermeability, given the crushing of the multi-layer structure in the plane of welding, which usually causes layers of one element

to be folded down onto that of the welded element and the internal layer of each element to be welded to that of the other element. This then generally results in a discontinuity in the barrier layer of the structure of the hollow body produced, giving rise therefore to a preferred path for liquid and vapour leakages.

Japanese Patent Application No. JA-63/1/8931, which describes joining planes resulting from the assembly of multi-layer structures in which the ends of the barrier layers meet at a point inside the welded seam, is known.

The impermeability obtained with such joints is not, however, yet good enough to comply with the very low limits imposed by the new standards, given the difficulties there are in maintaining contact between the end of the barrier layers of each element along the entire length of the run of welding.

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It is an object of the invention to provide a hollow body which has a level of permeability at the welding planes which is appreciably lower even than that obtained with the known methods based on a search for contact between the end of the barrier layers and which can meet the requirements imposed by the new environmental standards.

To this end, the invention relates to a hollow body made of plastic of multi-layer polymeric structure, comprising at least one internal barrier layer which is impermeable to gases and to liquids, in which body at least two elements of similar structure are welded together, characterized in that the welded elements are extended towards the outside of the hollow body by an appendage comprising the barrier layers.

"Hollow body" is intended to denote any structure, the surface of which has at least one empty or concave

part. As a preference, the hollow body here denotes a closed structure intended to contain a liquid and/or a gas. Particular preference is given to reservoirs and tanks. The hollow body may have orifices pierced in its envelope and allowing communication with the external environment. In general, the hollow body has a maximum of 10 orifices. Tubes are usually excluded from the hollow bodies according to the invention.

"Plastic" is intended to denote any material containing 10 one polymer. Thermoplastic polymers least preferred. The term "polymer" is intended to denote both homopolymers and copolymers (particularly binary or ternary ones). Examples of such copolymers are, 15 without implying any limitations: random copolymers, from sequenced polymerization, copolymers block copolymers and graft copolymers.

The thermoplastic polymers also comprise thermoplastic elastomers and blends thereof.

Any type of thermoplastic polymer or copolymer whose melting point is below the breakdown temperature is suitable. Synthetic thermoplastics which have a melting range spread over at least 10°C are particularly well-suited. Examples of such substances are those which have a polydispersion of their molecular mass.

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In particular, the hollow body may contain polyolefins, 30 graft polyolefins, thermoplastic polyesters, polyketones, polyamides and copolymers thereof.

A polymer often present in the hollow body is polyethylene. Excellent results have been obtained with high density polyethylene (HDPE).

A copolymer often used is the ethylene-vinyl alcohol (EVOH) copolymer. A blend of polymers or copolymers may also be used, as may a blend of polymeric substances

with inorganic, organic and/or natural fillers such as, for example, but without implying any limitation: carbon, inorganic salts and other inorganic derivatives, natural or polymeric fibres.

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According to the invention, the plastic of the hollow body is of a multi-layer polymeric structure. Such multi-layer structures consist of polymeric layers stacked and secured together containing at least one of the polymers or copolymers described above. They may be obtained using a coextrusion head or using a technique of completely or partially covering a substrate layer with one or more other layers. An example of the covering technique is the spraying of thermoplastic onto the substrate layer using a spray gun.

The hollow body according to the invention contains at least one barrier layer. This layer is on the inside of the multi-layer polymeric structure and therefore surrounded on both sides by at least one layer of plastic, the barrier properties of which are weaker. Usually, the layers situated on either side near a barrier layer have somewhat insignificant barrier properties.

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"Barrier layer" means a layer which is impermeable to gases and to liquids. It generally contains a barrier resin. Any known barrier resin may be present in the hollow body, provided that it is effective with respect to the fluids likely to be in contact with this hollow body, particularly hydrocarbons, and provided that it is compatible with the technique used to manufacture the multi-layer structure.

Non-limiting examples of possible resins that may be mentioned are polyamides or copolyamides and random copolymers of ethylene and of vinyl alcohol. A blend of different barrier resins is also possible. Very good results have been obtained with a hollow body

containing a barrier resin made of a random copolymer of ethylene and of vinyl alcohol.

According to the invention, the hollow body comprises at least two elements welded together. "Element" is to be understood as meaning any component or any part of a component of multi-layer polymeric structure, the shape of which has a flat surface or a surface at least part of which is concave. As a presence, the hollow body comprises a number of elements not exceeding 10. Particular preference is given to the hollow body comprising a maximum of 5 elements. A hollow body with two elements welded together has given excellent results.

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According to the invention, the elements are of similar structure. What this means is that the structure of each of the elements comprises a number of layers differing from one another by no more than three units and, as a preference, by no more than two units, and that the natures of the polymers involved in the layers which correspond with one another on each side of the welding surface are compatible from the chemical point of view and from the point of view of their ability to be assembled by welding. Preference is given to a hollow body in which the elements have structures with the same number of layers. Particular preference is given to the hollow body in which the elements have identical structures. In this case, the elements of identical structure may come from different components. Alternatively, they may just as easily come from parts of one and the same component. This last situation is encountered when the elements come from parts of one and the same parison made of plastic of multi-layer structure.

The hollow body according to the invention comprises welded elements, that is to say elements assembled edge to edge and secured by welding. The elements may be

welded along the entirety of their perimeter. Examples of this situation are hollow bodies consisting of distinct welded elements, and also hollow bodies consisting of a single parison gripped and welded along its entire periphery. In this situation, the hollow body elements according to the invention are generally welded over at least 80% of their perimeter. Another example of such hollow bodies are those which have at least one orifice situated in the perimeter of the welded elements. A preferred hollow body comprises elements welded along the entirety of their perimeter.

Alternatively, the elements may also be welded only over an insubstantial part of the perimeter of the hollow body. In the case of elements originating from a single parison, these elements may be welded only in two regions each near to one end of the parison. In this situation, the hollow body elements are generally welded over at least 5% of their perimeter.

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According to the invention, the hollow body comprises welded elements which extend towards the outside of this hollow body. The extension originates near the weld between two elements and extends towards the outside in the form of an appendage which contains the barrier layers of each element.

This appendage forms an integral part of the hollow body of which it constitutes a functional part.

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It may be in various forms. As a preference, its base anchored in the hollow body has a broader cross section than its end. It is often in the form of an outgrowth, of which the base, if sectioned on a plane perpendicular to the surface of the hollow body and to the welding kerbs, has a triangular cross section. It often terminates, at the end outside the hollow body, in a flattened blade containing the barrier layers.

The length of this appendage is such that the path to cross it between the barrier layers is long enough to reduce to a very low value the amount of liquid and/or gas that can pass through in a given time. preference, the appendage has a length of at least 0.2 mm. The "length" of the appendage is meant to mean the length of the line of intersection of the surface face of this appendage with perpendicular to the surface of the hollow body and to the welding kerbs at a point centred on the base of the appendage. As a preference, the length of the appendage is at least 5 mm. Usually, this length does not exceed 60 mm. The length of the appendage does not have to be uniform at every point. An advantageous appendage is that one which is longer in certain particular regions of the surface of the tank, at points where there is no problem of space occupancy dictating compliance with a maximum size.

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As a preference, these welded elements are extended by 25 an appendage over the entirety of the exterior periphery of the hollow body.

In addition to the barrier layers of each element, the appendage may also contain, in the hollow body according to the invention, at least one polymeric layer of a nature similar to that of one of the other layers present in each element, on any side of a barrier layer.

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similar to that of one of the other layers present in each element are to be found in the appendage. As a particular preference, the appendage contains, in addition to the barrier layers of each element, an even number of layers which correspond with one another in pairs in each element, these being arranged in the same sequence as in the element from which they originate. An advantageous variant of the appendage contains all the layers of each element.

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The appendage may be arranged in any way with respect to the exterior surface of the hollow body. As a preference, it is folded down so as to reduce the space occupancy of the hollow body. An advantageous variant of the hollow body according to the invention is the one in which the appendage is folded down against the exterior surface of the hollow body. This fold is on any side of the weld, onto any one of the elements of the hollow body.

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According to this variant, one possible hollow body is the hollow body in which the appendage is secured to the exterior surface of the hollow body against which it is folded down. Any type of securing is appropriate. One example of securing which has given good results is welding. In this case, the securing may be performed along the entire periphery of the hollow body. As a variant, it can just as easily be done only on a single or multiple part of this periphery. In the parts of the periphery of the hollow body where it is done, securing may also be effective over the entire surface of the appendage in contact with the hollow body. It may just as easily, as a variant, be performed only in a region near the end of the appendage.

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The hollow body according to the invention is particularly well suited to forming a tank. More specifically still, it is well suited to containing a liquid and/or gaseous fuel.

The invention also relates to a method for manuracturing, using the compression-moutding technique, a hollow body made of plastic of multi-layer polymeric structure comprising a barrier layer that is a barrier to liquids and to gases, by welding at least two elements together, whereby:

- a) the elements are inserted in an open multi-part mould,
- b) at least part of the ends of the elements which are to be assembled are gripped between the welding kerbs arranged at the periphery of at least two mould parts, so as to superpose them,
 - c) the mould parts are pressed together so as to weld the elements together by closing the mould, and, at the same time,
 - d) at least the barrier layers of the structure of these elements are forced to flow into a shallow and broad slot delimited by a space separating two mould parts near the welding kerbs and the cross section of which narrows at the end nearest the outside of the mould cavity,
 - e) the mould parts are continued to be pressed together so as to form an appendage which emerges from the surface of the hollow body on the outside of the mould cavity,
 - f) the mould is opened,
 - g) the hollow body thus produced is extracted from the mould.

In this method, the terms which are common have the same meaning as those given above in the description of the hollow body.

The method according to the invention makes use of a multi-part mould. This mould has all the characteristics of the moulds conventionally used in the compression-moulding technique.

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In this method, the "welding kerbs" are to be understood as being regions arranged at the periphery of part of a mould and capable of trapping and pressing together the corresponding edges of two elements that are to be welded, through collaboration with the corresponding peripheral region of another mould part when these parts are brought closer together by closing the mould.

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According to a preferred variant of the method according to the invention, the elements are also shaped inside the mould. A choice method for performing this shaping consists in injecting a blow-moulding fluid into the mould so as to press the elements against the walls thereof. Any gaseous or liquid fluid is suitable, provided that it is compatible with the elements that are to be welded and with the material of which the mould is made. Pressurized air has given good results.

According to the method according to the invention, including in its variant described hereinabove, it is also possible, having opened the mould at the end of assembly, to fold the appendage down against the surface of the hollow body. This operation may be performed directly in the open mould, the hollow body still resting in a mould part. It may also be performed when the hollow body has been completely extracted from all the parts of the mould.

The appendage may also be secured to the exterior surface of the hollow body once it has been folded down against this surface. One securing method which has given good results is to weld the appendage to the exterior surface of the hollow body.

The length of the appendage may be left as obtained by manufacture. It may also be normalized to a certain

value by trimming off any excess. In general, the appendage is not trimmed to shorter than a length of 0.2 mm. As a preference, this appendage is not trimmed to shorter than 5 mm in length.

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The method according to the invention, including all its variants, is very suitable for producing a fuel tank made of plastic of multi-layer polymeric structure.

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The invention finally relates to a compression-blow-moulding mould formed of at least two distinct parts comprising, at their periphery, welding kerbs capable of gripping and welding distinct elements made of plastic of multi-layer polymeric structure, in which the welding kerbs of two mould parts facing one another leave between them, when the mould is closed, a space the height of the cross section of which decreases towards the outside of the mould cavity and is extended by a shallow and broad slot intended to greatly compress the plastic while the mould is being closed.

In this mould, the terms which are common have the same meaning as the meaning given above in the description of the hollow body.